

Deformation and Orientation of Liquid Crystalline and Semi-crystalline Block Copolymers

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Beamline(s): X27C

Introduction: The orientation of poly(styrene-*b*-isoprene/LC) {P(S-*b*-ILC)} side group liquid crystalline diblock copolymers by oscillatory shear was studied as functions of temperature, shear frequency and strain for lamellar, PS cylinder and PI-LC cylinder samples of 126, 80 and 231 kDaltons/mol respectively. The morphology of analogs of the above materials produced by using hydrogen bonding instead of covalent bonding to attach mesogens to a block copolymer backbone was studied.

Methods and Materials: P(S-*b*-ILC) samples were cast and oriented by shearing in a shear cell modified for in-situ collection of scattered x-rays. The orientation was carried out below the clearing temperature of the LC and then slightly above the clearing temperature. For the hydrogen bonded samples, P(S-*b*-AA), the shear cell was also used to impart some orientation to the samples, and temperature was varied to study the phase behavior of these new materials.

Results: Results indicated that the mesophase for the covalently bound P(S-*b*-ILC) samples was smectic A in all cases, and that the mesogens aligned parallel to the inter-material dividing surface of the block copolymer (homogeneous anchoring). A unique transverse orientation was found in the cylindrical samples in which the cylinder long axes aligned along the neutral direction, such that the smectic layers were in the perpendicular orientation, with their layer normals also along the neutral direction, consistent with the homogeneous anchoring of the mesogens at the IMDS¹. This transverse orientation was at $T < T_{\text{SmA-isotropic}}$ of the LC and transitioned to the commonly observed parallel orientation when temperature was increased to $T > T_{\text{SmA-isotropic}}$. For the P(S-*b*-AA) hydrogen bonded system, homeotropic anchoring was observed – i.e. the mesogens oriented perpendicular to the inter-material dividing surface. This was probably the result of the greater mobility afforded these mesogens due to a longer spacer between the rigid unit and the acrylic acid host block. Samples of homopolymer acrylic acid complexed with the mesogen were also studied. Here, it is postulated that the mesogens force a microphase separation of uncomplexed portions of the backbone from complexed portions due to crystallization induces clustering of the mesogens along the polymer backbone. Evidence for this was recorded with the coincidence of a crystallization event in WAXS with the emergence of the 11 nm layer-type scattering in SAXS, displayed in Figure 1.

Conclusions: Highlight this text and type over it with any conclusions you may have or delete this line

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References:

1. Osuji C, Zhang Y, Mao GP, Ober CK, Thomas EL. *Macromolecules* 1999; 32:7703-7706.

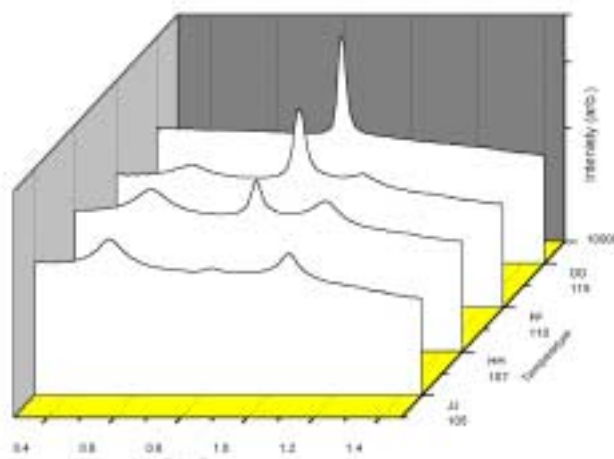


Figure 1. SAXS(T) for a 5.2k hPAA complexed with 0.50M of a hydrogen bonding biphenyl based mesogen. The lamellar peaks at 11 and 5.5nm emerge on cooling from 115 °C starting at about 110 °C